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⑯ **high temperature creep resistant thermoplastic elastomer compositions.**

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Description**Background and Statement of the Invention**

In EP-A 72 203, a method is described for producing a partially cross-linked rubber-resin composition by melting and mixing a peroxide-curable olefin copolymer rubber and a peroxide-decomposing polyolefin resin with an organic peroxide compound. The rubber in particulate form and the resin and peroxide are fed to a twin screw extruder and the rubber and the resin are thereby subjected to dynamic heat treatment in the presence of the peroxide.

Examples of the peroxide-curable olefin copolymer rubber include ethylene [1-butene] non-conjugated diene terpolymer rubber. Examples of the peroxide-decomposing polyolefin resin include crystalline polypropylene. Among other additives are mentioned mineral oil softener, and peroxide-non-curable hydrocarbon rubbers such as polyisobutylene and butyl rubber. The EP-A 72 203 does not specify a use for the partially cross-linked rubber-resin compositions.

French Patent Specification FR-A 2 514 016 describes polyolefin compositions stable to gamma irradiation containing a hindered amine stabilizer. Syringes or other medical components can be made from such compositions and sterilized by the use of gamma irradiation.

Generally speaking, this invention relates to elastomer compositions for use in preparing objects such as stoppers to be placed in syringes, and evacuated tubes such as Vacutainer brand evacuated tubes, a product of Becton, Dickinson and Company, Paramus, New Jersey 07652. Such tubes have a vacuum applied to them and it is important that that vacuum be maintained during storage life, and use of the evacuated container. For the syringes, it is important that the stoppers maintain sealing engagement with the cooperating walls of the syringe tube. These products, sterilized either by Ethylene Oxide or by high energy radiation are sold in the market as sterile product. However, resterilization of these devices by autoclaving is practiced by the users.

Currently, vulcanized elastomers such as natural or butyl rubber are used for making the above products. Although the vulcanized elastomers provide autoclavability or stability at elevated temperatures there are certain drawbacks in comparison with thermoplastic elastomers. Various additives must be incorporated into vulcanized elastomers making them prone to toxicity, whereas less additives are required to produce a thermoplastic elastomer. Vulcanized products are process (molding) limited and labor intensive, whereas thermoplastic elastomer products can be fabricated in different processes making them more economically attractive. However, although thermoplastic elastomers behave as vulcanized elastomers at room temperature, their properties at elevated temperatures rapidly change. At high temperatures, thermoplastic elastomers will creep more than the vulcanized materials. The state-of-the-art of this invention is that the said composition is medically clean, capable of

fabrication in any molding process, and will maintain required sealing properties at elevated temperatures such as are seen in autoclaving. Thus, attempts have been made to develop synthetic elastomer compositions which may be substituted for natural rubber in preparing stoppers for such items as evacuated tubes for the collection of medical samples, and for syringe stoppers for the administration of various medications. Other applications where the sealing properties of synthetic elastomers are of importance include O-rings, and hoses carrying high temperature fluids including steam lines and automotive applications.

While a variety of different compositions have been developed which will provide the appropriate resiliency required to maintain proper seal, as discussed above, such compositions will not always tolerate the elevated temperatures required to bring about the proper autoclaving sterilization of the containers. As a result, even though the stoppers provide appropriate vacuum and/or sealing prior to such sterilization, the high temperatures have a tendency to break down the elastomer composition to the degree where high compression set takes place, so that after a period of storage life, the stoppers leak or in other ways fail in their use.

Attempts have been made to deliberately modify elastomer compositions in order to make them resistant to autoclave temperatures. Representative compositions for providing autoclavable elastomer compositions are taught, for example in U.S. Patents 4,210,686 and 4,440,815. However, the compositions taught in those patents, while providing appropriate resistance to autoclave temperatures, are not compositions which will produce objects, such as stoppers, which are placed under stress when they are put into the position of use, and then autoclaved under the stress conditions. That is, as will be understood by practitioners-in-the-art, stoppers placed in evacuated tubes or used as stoppers and/or pistons movable in syringes are placed under stress. The imposed stress during the period of autoclaving exposure to high temperatures, has the effect of generating creep by breaking down the elastomer composition and causing resulting failures in storage and in use.

With this invention, by contrast, compositions are provided which provide elastomeric objects which withstand, simultaneously, the effects of autoclaving temperatures, and the stress placed on the objects during the period of time when they are being autoclaved. Thus, stoppers produced from the compositions, in accordance herewith, will maintain their proper sealing characteristics during the storage life of the evacuated containers and/or syringes so that they are useful when they are selected to be used in medical applications, for example. This is so even though such objects have been exposed to the elevated temperatures required for autoclaving.

With the foregoing and additional objects in view, this invention will now be described in more detail and other objects and advantages will be apparent from the following description.

A thermoplastic elastomer composition capable of

withstanding autoclave temperatures, the composition being creep resistant when autoclaved under stress is formulated in accordance with the principles of this invention by combining dynamically vulcanized ethylene-propylene-diene terpolymers and polypropylene as the principle component, together with a butyl based rubber such as butyl rubber, halogenated butyl rubber, or partially cross-linked butyl rubber. A stabilizer is added to the composition in the form of a hindered amine such as, for example, bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate. As a processing aid for the composition, in accordance herewith, polyisobutylene plasticizer is added.

The principle component comprised of the dynamically vulcanized ethylene-propylene-diene terpolymer (EPDM) and polypropylene is present within the range of between 65 and 90 percent, and preferably within the range of between 65 and 75 percent by weight. The second major component of the composition, in accordance herewith in the form of a butyl based rubber such as butyl rubber, halogenated butyl rubber or partially cross-linked butyl rubber is present within the range of between 5 and 20 percent by weight, and preferably within the range of between 10 and 15 percent by weight. The hindered amine is present in the amount within the range of between 0.01 and 5.0 percent by weight, and preferably 0.1 and 0.5 percent by weight, whereas the polyisobutylene, a processing aid, is present within the range of between 1 and 20 percent by weight, and preferably 3 and 18 percent by weight. In this connection, it should be understood that the polyisobutylene is utilized as a plasticizer.

The principle component comprised of cured EPDM and polypropylene PP may be obtained as Santoprene (Trade Mark), a product of Monsanto Chemical Corporation. The hindered amine stabilizer may be Tinuvin (Trade Mark), a product of Ciba Geigy, while the plasticizer may be Vistanex (Trade Mark) MML-80 or MML-100, a product of Exxon Corporation.

It is believed that the cured EPDM of the principle component EPDM/PP does not undergo a significant permanent deformation under stress and elevated temperature for autoclave conditions, which are, for example, 270° Farenheit (say 132°C) for 15 minutes. However, the PP of this composition does. Therefore, the EPDM/PP is blended with the second component, in the form of butyl rubber, for example, which is a gum rubber. The high temperature gum rubber prevents the polypropylene from permanently deforming at autoclave temperature, thus maintaining elasticity of the final elastomer, in accordance herewith, and also higher viscosity than the polypropylene. The gum rubber acts, therefore, as a damping agent for the polypropylene. The molecules of the gum rubber are so compactly arranged that they show high damping characteristics at elevated temperatures required for autoclave conditions. By contrast, at molding process temperatures of 400° Farenheit (say 204°C) all of the components will melt and flow without any degradation. Thus, the composition can be processed under injection, compression, extrusion or blowmolding con-

ditions.

As representative of one procedure for preparing a composition in accordance with this invention, one may note the following examples reciting representative procedures for formulating such a composition. It is to be understood, however, that these examples are being presented with the understanding that they are to have no limiting character on the broad disclosure of the invention as generally set forth herein, and as directed to those skilled in the art.

EXAMPLE I

15 1000 grams of Santoprene® were introduced into an internal mixer maintained at a temperature of 400°F (about 204°C) and allowed to mix for five minutes. Thereafter, 50 grams of polyisobutylene was admixed with the Santoprene®, and the mixture was 20 blended for 10 minutes. The polyisobutylene acts as a plasticizer for the resulting composition. Then, 150 grams of a butyl rubber composition were added and the resulting mixture was blended for five minutes. In this connection, the butyl rubber may be introduced prior to the plasticizer. Finally, 1.155 grams of Tinuvin® 770 was added, and the final mixture was 25 blended for 5 minutes. Then, the resulting blended mixture was injection molded to produce 10 dozen 10 cm³ stoppers for use in syringes. The stoppers were 30 then subjected to creep measurement before and after autoclave conditions. The strain was calculated by measuring the stopper outside diameter, the syringe barrel internal diameter, and the contact area of the stopper. After autoclaving at 270°F (about 132°C) for 15 minutes the residual strain in 35 each stopper was calculated to be substantially 30 percent of the initial strain, well within the requirements necessary to maintain the required seal for passing conventional leakage tests for syringes.

EXAMPLE II

40 1000 grams of Santoprene® were introduced into an internal mixer maintained at a temperature of 400°F (about 204°C) and allowed to mix for five minutes. Thereafter, 35 grams of polyisobutylene was 45 admixed with the Santoprene, and the mixture was blended for five minutes. Then 100 grams of a polyisobutylene-isoprene copolymer composition was 50 added, and the resulting mixture was blended for five minutes. Finally, 1.125 grams of Tinuvin® 770 was 55 added, and the final mixture was blended for five minutes. Then, the resulting blended mixture was injection-molded to produce ten dozen 10 cm³ stoppers for use in syringes. The stoppers were 60 placed in conventional syringes and the iso leakage test was conducted before and after autoclaving. The autoclaving was performed at 270°F (about 132°C) for 15 minutes. The syringes of interest 65 passed the leakage testing in this operation. Needless to say, the stoppers provide superior gas barrier properties, which is of interest in applications using stoppers in evacuated tubes.

Accordingly, and as will be apparent from the foregoing, there are provided in accordance here-

with methods and compositions for imparting simultaneously to elastomers properties which enable the elastomers to withstand the effects of elevated temperatures required for autoclaving while the objects comprised of the elastomer are placed under stress. Thus, the objects may be formed, placed in the position in which they are to be used under stress and then autoclaved and the objects will maintain their proper elasticity, as required for use. There is no substantial degradation or breakdown in the properties of the objects formed from the compositions, in accordance herewith so that they maintain their properties over a period of time required for shelf life of the objects in which they are used such as evacuated tubes for taking blood samples and syringes for use in various medical applications. These various medical devices may be constructed and autoclaved and they will maintain their sealing properties over a long period of time.

While the methods and compositions herein disclosed form preferred embodiments of the invention, this invention is not limited to those specific methods and compositions and changes can be made therein. For example, a variety of uses for the elastomers of the invention will be apparent to the practitioner-in-the-art where high temperatures are involved in combination with constant sealing requirements. Such applications include high temperature, high pressure steam and water lines, as well as O-rings, labyrinth and other sealing applications.

Claims

1. A thermoplastic elastomer composition capable of withstanding autoclave temperatures wherein the composition is creep resistant when autoclaved under stress and contains:-

- (a) 65 to 90 percent by weight of a mix of dynamically vulcanized ethylene-propylene-diene terpolymer and polypropylene,
- (b) 5 to 20 percent by weight of a butyl based rubber,
- (c) 0.01 to 5.0 percent by weight of a hindered amine stabiliser,
- (d) 1 to 20 percent by weight of a polyisobutylene plasticizer.

2. A composition according to claim 1 wherein the mix (a) of dynamically vulcanized ethylene-propylene-diene terpolymer and polypropylene is present in the range of 65 to 75 percent by weight.

3. A composition according to any of the preceding claims wherein the butyl based rubber (b) is present in the range of 10 to 15 percent by weight.

4. A composition according to any of the preceding claims wherein the butyl based rubber (b) is selected from butyl rubber, halogenated butyl rubber, partially cross-linked butyl rubber and polyisobutylene-isoprene copolymer.

5. A composition according to any of the preceding claims wherein the hindered amine (c) is present in the range of 0.1 to 0.5 percent by weight.

6. A composition according to any of the preceding claims wherein the hindered amine (c) is bis [2, 2, 6, 6-tetramethyl-4-piperidinyl] sebacate.

- 7. A composition according to any of the preceding

claims wherein the plasticizer (d) is present within the range of 3 to 18 percent by weight.

8. A shaped, autoclavable object made from a composition according to any of the preceding claims.

9. An object according to claim 8 wherein the object is a stopper for a syringe or evacuated tube.

Patentansprüche

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1. Thermoplastische Elastomerzusammensetzung, die in der Lage ist, Autoklaventemperaturen standzuhalten, wobei die Zusammensetzung, wenn sie im Autoklaven behandelt wird, kriechbeständig unter Beanspruchung ist und enthält:

- (a) 65 bis 90 Gew.-% eines Gemisches von dynamisch vulkanisiertem Ethylen-Propylen-Dien-Terpolymer und Polypropylen,
- (b) 5 bis 20 Gew.-% eines Kautschuks auf Butylbasis,
- (c) 0,01 bis 5 Gew.-% eines sterisch gehinderten Aminstabilisators und
- (d) 1 bis 20 Gew.-% eines Polyisobutyleneichmachers.

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2. Zusammensetzung nach Anspruch 1, wobei das Gemisch (a) aus dynamisch vulkanisiertem Ethylen-Propylen-Dien-Terpolymer und Polypropylen im Bereich zwischen 65 und 75 Gew.-% vorhanden ist.

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3. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei der Kautschuk auf Butylbasis (b) im Bereich zwischen 10 und 15 Gew.-% vorhanden ist.

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4. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei der Kautschuk auf Butylbasis (b) gewählt ist aus Butylkautschuk, halogeniertem Butylkautschuk, partiell vernetztem Butylkautschuk sowie Polyisobutylene-Isopren-Copolymer.

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5. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das sterisch gehinderte Amin (c) im Bereich zwischen 0,1 und 0,5 Gew.-% vorhanden ist.

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6. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das sterisch gehinderte Amin (c) Bis-[2,2,6,6-tetramethyl-4-piperidinyl]-sebacat ist.

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7. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei der Weichmacher (d) im Bereich von 3 bis 18 Gew.-% vorhanden ist.

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8. Geformter autoclavierbarer Gegenstand, hergestellt aus einer Zusammensetzung nach einem der vorhergehenden Ansprüche.

9. Gegenstand nach Anspruch 8, wobei der Gegenstand ein Stöpsel bzw. Stopfen für eine Spritze oder eine evakuierte Röhre ist.

Revendications

1. Composition d'élastomère thermoplastique capable de résister aux températures de l'autoclave, cette composition résistant au fluage lorsqu'elle est traitée à l'autoclave sous contrainte et contenant:

- (a) 65 à 90% en poids d'un mélange de terpolymère d'éthylène-propylène-diène, soumis à une vulcanisation dynamique, et de polypropylène,

(b) 5 à 20% en poids d'un caoutchouc de type butyl,
(c) 0,01 à 5,0% en poids d'une amine empêchée stabilisante, et
(d) 1 à 20% en poids d'un polyisobutylène plastifiant.

2. Composition selon la revendication 1, dans laquelle le mélange (a) de terpolymère d'éthylène-propylène-diène, soumis à une vulcanisation dynamique, et de polypropylène est présent dans la gamme de 65 à 75% en poids.

3. Composition selon l'une quelconque des revendications précédentes, dans laquelle le caoutchouc de type butyl (b) est présent dans la gamme de 10 à 15% en poids.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le caoutchouc de type butyl (b) est choisi parmi un caoutchouc butyl, un caoutchouc butyl halogéné, un caoutchouc butyl partiellement réticulé et un copolymère de poly(isobutylène-isoprène).

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'amine empêchée (c) est présente dans la gamme de 0,1 à 0,5% en poids.

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'amine empêchée (c) est le sébacate de bis[2,2,6,6-tétraméthyl-4-pipéridinyle].

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle le plastifiant (d) est présent dans la gamme de 3 à 18% en poids.

8. Objet façonné pouvant être traité à l'autoclave fait d'une composition selon l'une quelconque des revendications précédentes.

9. Objet selon la revendication 8, qui est un bouchon pour une seringue ou un tube sous vide.

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